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A SHOCK TUBE STUDY OF THE H2/02/CO/AR AND H2/N20/CO/AR SYSTEMS.(U)
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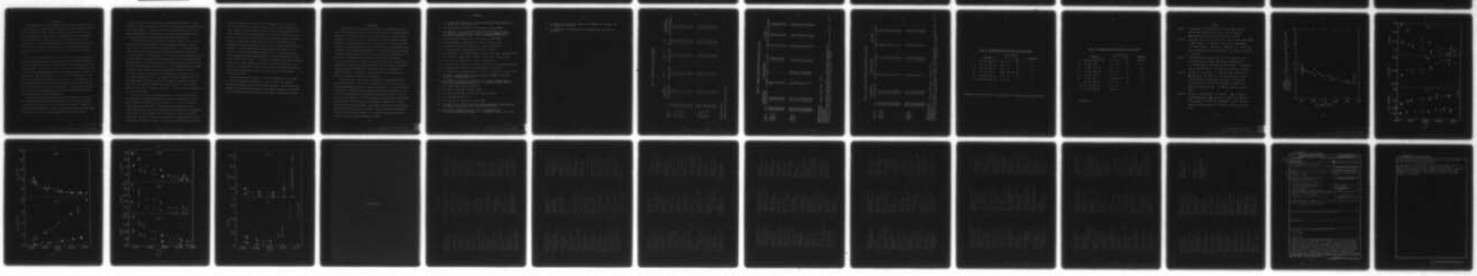

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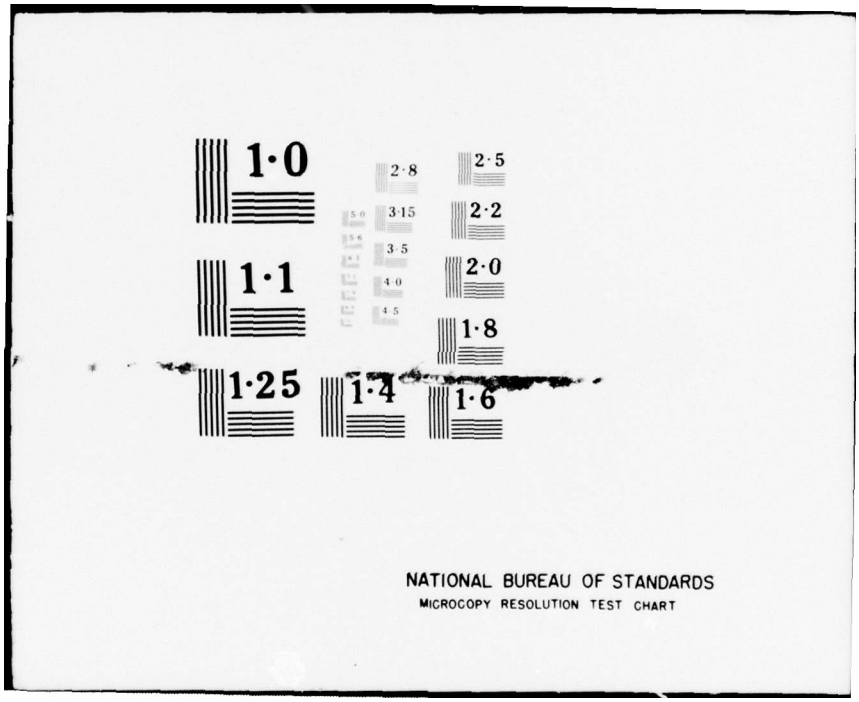
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PROJECT SQUID
TECHNICAL REPORT UMO-2-PU

A SHOCK TUBE STUDY OF THE $H_2/O_2/CO/Ar$ and $H_2/N_2O/CO/Ar$ SYSTEMS

BY

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$H_2/O_2/CO/Ar$ and $H_2/N_2O/CO/Ar$ SYSTEMS

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Abstract

Emissions at 450 nm and 4.27 μm have been measured when a variety of mixtures containing H_2, CO, either O_2 or N_2O, and Ar were heated behind reflected shock waves to temperatures of 2000-2850 K and total concentrations near $5x10^{18}$ molecule/cm^3. These emissions were used to obtain absolute concentration - time data for both oxygen atoms and carbon dioxide. The data were then compared to the results of numerical integrations of the likely mechanisms. It was observed that quantitative agreement between calculations and observations were obtained for the $H_2/CO/O_2/Ar$ system using recent high temperature literature rate constants. For the $H_2/CO/N_2O/Ar$ system, the rate constant for the reaction:

$$H + N_2O = N_2 + OH$$

was adjusted so as to fit the data. Here it was found that a good fit to both [O] and [CO_2] profiles could be achieved with $k = 3.0x10^{-9} \exp(-113kJ/RT)$ cm^3 $molecule^{-1}$ s^{-1}. Comparison to data at lower temperatures suggests that this might be another example of a "non-Arrhenius" rate constant. The implications of these results to studies of hydrocarbon oxidation are discussed.

INTRODUCTION

The study of oxidation reactions in shock tubes has been stimulated by the use of fast, accurate numerical integration routines. Now it is possible for kineticists to more definitively test various oxidation mechanisms by a detailed comparison of calculated and observed concentration - time profiles. The utility of the approach has been discussed by Schott and Getzinger [1] in their review of the H_2/O_2 system. Although the $H_2/O_2/CO$ system has also been successfully studied by this approach [2,3], extension to even simple hydrocarbon systems like CH_4/O_2 has been limited by lack of reliable high temperature rate constants. A common practice has been to extrapolate low temperature flow system data to the temperature range of interest. Unfortunately this approach can lead to serious errors; recent studies [4-10] have convincingly demonstrated that many reactions of importance in combustion mechanisms exhibit markedly "non-Arrhenius" rate constants. In this light it appears to be most desirable to measure rate constants *in the same high temperature regime* where they will be used to test the combustion mechanisms. However, it is equally important that these data be obtained from relatively simple systems where assignment of the desired rate constant is not contingent upon proper assignment of a complex mechanism and the associated rate constants.

One such system results from the substitution of N_2O for O_2 in combustion studies. Recent work in this laboratory [11] showed that N_2O is a particularly useful source of oxygen atoms between 2000-3000 K. Thus a study of combustion systems where N_2O replaced O_2 should provide useful information about rates of oxygen atom reactions at high temperatures. The primary advantage of N_2O as an oxidant is that oxygen atom reactions will occur in an environment where the concentration of molecular oxygen is much less than a normal combustion system; this considerably simplifies the kinetic analysis. Prudence dictates that such

a substitution first be tested on a known system. This paper reports the results of such a test. Data are given for an extensive series of experiments on both the $H_2/O_2/CO/Ar$ and $H_2/N_2O/CO/Ar$ systems. The results obtained in the $H_2/O_2/CO/Ar$ system coupled with those obtained earlier on N_2O dissociation serve to characterize most of the reactions of importance in the $H_2/N_2O/CO/Ar$ system. If the N_2O system profiles yield a value for the rate constant of the reaction $O + H_2 \rightarrow OH + H$ consistent with that obtained from the much more extensively studied O_2 system, it would suggest that the N_2O mechanism is appropriate and that N_2O substitution might indeed be a useful technique for obtaining high temperature oxygen atom rate constants.

EXPERIMENTAL

The 7.6 cm shock tube, gas handling system, and optical configuration have been described previously [11]. Infrared emissions were first collimated by two slits 1.5 mm wide and 5 mm high placed 50 mm apart before passing through a 4.27 μm interference filter (FWHM = 0.18 μm) and being focussed upon a liquid-nitrogen-cooled InSb detector. Visible emissions were monitored by a RCA 1P28A/V1 photomultiplier mounted behind a 450 nm interference filter (FWHM = 6.5 nm) and two 1 mm wide by 2 mm high slits 38 mm apart. The signals from the photomultiplier were collected with a Biomation Model 805 transient recorder at 0.5 μsec intervals. Infrared signals were monitored at 10.0 μsec intervals by a digital data acquisition system previously described [12]; the only change is that the Supernova computer has been replaced with a Motorola 6800 Microprocessor.

Gas mixtures were prepared manometrically using AIRCO Ar (99.9998%), CO_2 (99.999%), H_2(99.9995%), and N_2O (99.995%), Scientific Gas Products O_2 (99.999%) and Matheson CO (99.99%). The CO was slowly passed through a coil of copper tubing at 77 K before addition to the vacuum line. The other gases were used as supplied. The shock tube was typically pumped down to 2 mPa (1.5×10^{-5} torr) with an observed leak-outgassing rate of less than 2.5 mPa/min. Shocks were usually initiated approximately one minute after pump isolation so that the nominal background pressure was 5 mPa. The initial test section pressures were typically 2.7 kPa so that background impurities contributed $\sim$ 2 ppm which is comparable to the total impurity levels in the mixtures used. Helium was used as the driver gas in all experiments, and shocks were initiated by either spontaneous or manual rupture of Mylar diaphragms.

No-reaction shock conditions behind the reflected shock were obtained from measured incident shock velocities. There was little difference in conditions calculated using a constant velocity assumption and those where the measured

(small) velocity changes were extrapolated to the observation window. Usually these methods agreed within 25 K. Shocks which had differences of 50 K or more were rejected. Conditions reported in this paper used the assumption of constant velocities. Pressures computed with this assumption were in very good agreement with those measured in the plane of the observation windows by a pressure transducer. No corrections were made for non-ideal effects; the observed pressure profiles were always flat over the time interval that data were collected.

RESULTS

Visible Emissions. Systems containing oxygen atoms and carbon monoxide are known to emit visible radiation whose intensity is proportional to the concentrations of these species [13]. In these experiments this emission was monitored at 450 nm to attempt to minimize the contribution of extraneous emissions. This system was calibrated using the partial-equilibrium technique [13]. Here two mixtures of $H_2/O_2/CO/CO_2/Ar$ (See Table I) were heated behind reflected shock waves to 1970-2745 K and the flame-band emission recorded. This signal rapidly reached a constant intensity which was maintained for hundreds of microseconds. This constant signal arises from the quasi-equilibrium concentrations of the various species (including radicals) prior to the onset of recombination reactions. These concentrations are easily calculated from the well known equilibrium constants of the bimolecular reactions of interest. Note these experiments were done at relatively low total concentrations to minimize recombination. The observed constant signal and the fact that variation of the total concentration by a factor of two had no effect upon the signal levels were taken as evidence that the effect of recombination was negligible. Additional experiments near 5×10^{18} molecule/cm^3 indicated small but noticeable deviations suggesting that at that concentration the assumption of partial equilibrium is beginning to break down. The least square fit to the data in Fig. 1 yields an activation energy of 16.9 ± 2.7 kJ/mole. This can be compared to the value of 14.4 kJ/mole reported by Schott, et. al., [13] over the range 1300-2000 K. The data suggests this calibration factor is good to approximately 10%. With this factor, it is possible to determine the product [CO] [O] over the temperature interval by a simple measurement of the flame-band signal. Attempts to use this data to determine oxygen atom concentrations are complicated by the fact that there will be small changes in the CO concentration during an experiment.

To eliminate this ambiguity, the calibration factor was incorporated into the numerical integration scheme and was used to convert the computed [CO] [O] product to a computed flame-band voltage. This could then be compared directly to that observed; note this procedure allows for no normalization factors. In effect, given the small CO concentration changes (typically on the order of 5%) this approach yields absolute O-atom profiles.

Although the wavelength chosen for observations minimized the background emissions, it was not possible to completely eliminate them. For this reason, a preliminary series of experiments were performed which were similar in all respects to those listed in Tables II and III except that CO was omitted. Here the time-resolved emissions at 450 nm were recorded over a temperature range somewhat larger than that listed. This background data was fed into a two-dimensional array in the data reduction program. A bicubic spline interpolation routine was used to estimate the time-varying background at the temperature of a "real" experiment and this background was then subtracted from the total signal to yield the corrected flame-band signal. It was estimated the background obtained in this way was good to $\sim$ 10%. The background for the O_2 experiments was much smaller than for the N_2O shocks. Even for the N_2O case, the background was typically only 10% of the total signal.

In the N_2O experiments the flame-band signal was observed to increase rapidly upon passage of the reflected shock. In many instances the increase was so rapid that the observed signal was clearly affected by the finite slit width of the observation system. The slit effect was included in the numerical integration scheme by integrating the computed [CO] [O] product over the appropriate slit function. The detector efficiency was assumed to be unity for the 1.0 mm slit opening and then to drop linearly to zero at a distance 2.3 mm beyond each slit edge. In this way, the computed slit-modified flame-band signal could be

directly compared to that observed. Here it was convenient to define t_o as the time at which the reflected shock front was first visible to the detector. All visible data are reported with respect to t_o. Typically, t_o is $\sim$ 5 μsec earlier than t_{mp}, the time of shock front passage of the window midpoint.

Experimental observations of the flame-band signals are listed in Tables II and III. For the O_2 experiments, induction times were clearly evident. Here the induction time t_i is defined as the time at which the corrected flame-band signal equals 20 mv, which was the lowest signal which could be reproducibly extracted from the data. As one would expect, the t_i values for Mixture D are lower than those of C since here the CO concentration was larger. For C, t_i corresponds to an oxygen atom concentration of $\sim 1 \times 10^{15}$ molecule/cm^3; whereas in D the concentration is $\sim 2.5 \times 10^{14}$. In D the higher CO concentration made it possible to observe the exponential growth of the flame-band emission. In all cases it was possible to observe at least a decade of such growth and the slopes of these plots are listed in Table II where λ is defined as the slope of a plot of ℓn (flame-band signal) versus time. Similar plots for C yielded curves that were clearly concave downward, indicating the exponential growth region occurred at concentrations below the sensitivity level. At later times both mixtures exhibited a constant signal which is listed in Table II as V_{max}.

The flame-band signals from the N_2O system were characterized in terms of $t_{½}$ and V_{max}. Here $t_{½}$ was defined as the time (again relative to t_o) when the signal had reached one-half its plateau value of V_{max}. As one would expect, the nature of the flame-band signal is drastically different in the O_2 and N_2O cases. Figs. 2 and 3 illustrate this difference. Note that $t_{½}$ values for N_2O are even lower than t_i for O_2. Qualitatively such differences are expected; the oxygen atom concentration gets a "head start" in the N_2O system since N_2O

dissociation is faster than the initiation reactions in the O_2 case. Also note the marked difference in the temperature dependencies of V_{max}. In these Figures the error bars were computed with a standard propagation scheme and included contributions from uncertainties in the calibration (10%), background corrections (10%), and the measurement of the flame-band signal (5-10%).

Infrared Emissions. The total signal at 4.27 μm was corrected for emissions other than those due to CO_2 with a procedure similar to that used for the visible signal. Here a series of N_2O/CO/Ar as well as CO/Ar experiments were performed to determine the background. The corrected time-resolved data were then converted to CO_2 profiles via calibration factors obtained from a series of CO_2/Ar shocks. Parameters used to characterize these profiles are listed in Tables II and III. It was observed in both the N_2O and O_2 systems that the first data collected were at sufficiently long times to ignore possible slit effects. For ease of comparison to the calculations, all times recorded for the infrared data are with respect to t_{mp}, the time when the reflected shock reached the midpoint of the observation window. Note this convention is different from that used for the visible data where t_o was used. In general the CO_2 profiles for the O_2 system exhibited an induction time, quickly achieved a region of linear growth, and then gradually approached a constant (or slightly increasing) value. There was not sufficient temporal resolution to accurately characterize the region of increasing rate or the period of constant rate. The induction time was defined in the usual way as the t-axis intercept of the line which passed through the points exhibiting linear growth. Later points on the profile were characterized in terms of the time at which a particular CO_2 concentration was reached. Two of these times are listed in Table II and shown along with induction times in Fig. 4. The CO_2 profiles in the N_2O system were also characterized in terms of the times required to reach certain CO_2 concentrations. In general, CO_2 pro-

duction in the N_2O system was much more rapid than that observed in the O_2 system; no induction period was evident. At longer times, the CO_2 concentrations were generally smaller in the N_2O system than in the O_2 work. The differences were most pronounced at higher temperatures and in the 3% CO mixtures where the concentrations were lower by about a factor of three. The characteristic times are listed in Table III and shown in Fig. 5. In both Figs. 4 and 5, the error bars were calculated assuming 10% errors in the CO_2 calibration, 10% error in the background correction, and 1-5% error in the observed signal. The large error bars in some regions of Figs. 4 and 5 are due to the relatively small slopes in those particular profiles at certain times; here small calibration errors translate into large time uncertainties.

DISCUSSION

A likely mechanism for the $H_2/O_2/CO/Ar$ system includes the reactions listed in Table IV [2,14]. Fortunately the rate constants for many of these reactions have been extensively studied. Perhaps the most interesting result of recent work is the growing consensus that the high temperature measurements yield rate constants higher than one would expect by a simple extrapolation of the low temperature data. Thus an attempt was made to see if the above mechanism, using rate constants determined at high temperatures, was quantitatively consistent with the data reported herein. Table IV lists the rate constants used for this purpose.

This system of equations with the associated rate constants was numerically integrated using a program previously described [17]. The program was modified to use the flame-band calibration data to convert the [CO] [O] product to a corresponding voltage. The slit effect was also calculated as described earlier. The calculated flame-band and CO_2 profiles were then treated exactly as the experimental data to yield calculated values of the various reaction parameters. Results of the calculations are shown in Figs. 2 and 4. It is felt that the extent of agreement can be taken as additional evidence for the essential correctness of the mechanism and the rate constants chosen. It was particularly gratifying to observe such good agreement on an absolute scale for both observables over the entire time range of the observations.

Sensitivity tests were performed by varying the individual rate constants by a factor of two each way and observing the effect on the computed profiles. It was seen that this system is most sensitive to k_2, k_4, and k_5. Changes in one of these must be offset by a change in another to keep the calculations within the error bars. Since k_2 and k_4 were determined on systems where k_5 was

not involved, and the determination of k_5 was done under conditions to minimize the effect of other rate constants, there is clearly no justification for modifying these rate constants. It should be noted that the value used here for k_5 is in quite good agreement with that proposed in a recent review [7] and that k_2 and k_4 were obtained from an extensive study of the H_2/O_2 system [13,16].

A likely mechanism for the N_2O system is listed in Table V. This is similar to that used earlier for $N_2O/H_2/Ar$ systems [18-20] with the addition of the reactions of CO. Of particular note is that Reactions 1' - 3' have been studied under simpler conditions where specification of rate constants is relatively straightforward [11,21]. Also Reactions 2 - 6 can be carried over directly from the O_2 system where it was explicitly verified that these values were consistent with the present data. In this sense, one can approach the N_2O system with essentially only one unknown, namely the rate constant k_4'. Thus the approach taken was simply to attempt to find a value of k_4' which was compatible with all of the data. Preliminary calculations showed that the profiles were very sensitive to k_1' and very slight adjustments in k_1' ($\sim$ 10% change from the value reported in Ref. 11) noticeably improved both the V_{max} temperature dependence and the CO_2 profiles. Such a shift was compatible with the data reported in Ref. 11. This adjusted value of k_1' was used in subsequent calculations. These calculations now treated k_4' as the only variable.

There is very little high temperature data on k_4'; only one study [18] has reported values for temperatures above 2000 K [22]. Recently this reaction has been studied in a flow system over the interval 718 K $\leq$ T $\leq$ 1111 K [23] and in flames between 1000-1700 K [24]. The reported activation energies for this lower temperature work range from 55 kJ/mole [24] to 72 kJ/mole [23]; extrapolation of these results into the higher temperature regime thus leads to considerable uncertainty. A series of calculations suggested that the value obtained by extrapolating the flow tube work to 2450 K was in quite good accord with our data, but

that obvious problems were apparent at higher temperatures. In particular, calculated values of the flame-band plateau (V_{max}) were too high and there was a severe mismatch in the long time CO_2 profiles. Both of these features were improved significantly in both N_2O mixtures by increasing the value of k_4' by 50% at 2900 K. Furthermore, the overall temperature dependence of V_{max} is improved by using a value of k_4' at 2100 K somewhat lower than that obtained from an extrapolation of k_4' from the flow tube work. For this reason a value of k_4' was obtained by a simple pivoting about the extrapolated value at 2450 K. This yields $k_4' = 3.0 \times 10^{-9} \exp(-113 kJ/RT)$ $cm^3 molecule^{-1} s^{-1}$. Note this expression is only applicable over the range 1950-2850 K. The agreement obtained with this value is shown in Figs. 3 and 5. In addition it should be mentioned that detailed comparisons of computed profiles with particular experiments showed (in a vast majority of cases) that the calculated values for both flame-band and CO_2 signals were within the experimental error bars for the entire 500 μsec observation time for both mixtures.

The value reported here from k_4' is in very good agreement (14%) at 2000 K with the value suggested by Leeds [22]. However, at 2900 K this value has increased to be nearly a factor of three larger than Leeds. Such an increase was mandated by the observations, and this fact may indeed suggest that this reaction is one more addition to those recently discovered with "non-Arrhenius" behavior.

CONCLUSIONS

In this work emission signals have been related to the absolute concentration - time behavior of oxygen atoms and carbon dioxide over an extended range of conditions. These data provide a crucial test for any mechanism/rate constant combination. The ability of such a combination to accurately model all of these data would strongly suggest such a scheme is appropriate. In the O_2 system the mechanism is generally accepted and thus it was possible to test the best current estimates of the associated rate constants. The agreement observed can be taken as rather convincing evidence of the correctness of the rate constants used. In particular it reinforced the earlier observations that both the reactions $O + H_2 \rightarrow OH + H$ and $OH + CO \rightarrow CO_2 + H$ have rates well above what a simple extrapolation of low temperature data would suggest. This observation is critically important when one is attempting to choose rate constants for modeling of a combustion system; it is imperative that one be aware of the difficulties inherent in using data collected at low temperatures.

For the N_2O case it was possible to approach the system with most of the rate constants in hand. After a value was obtained for $H + N_2O \rightarrow OH + N_2$, no further adjustments were required to obtain a quantitative fit to the observations. In particular, it was observed that the profiles were quite sensitive to $O + H_2 \rightarrow OH + H$ and that the best fit was obtained with the same value which fit the O_2 system. In this respect it is felt this sequence of experiments has demonstrated that substitution of N_2O for O_2 is a useful method to measure rates of oxygen atom reactions at high temperatures. Furthermore, it appears that the postulated mechanism for the N_2O system is reasonable. This point should be very useful in the analysis of ongoing experiments in this laboratory where N_2O is being substituted for O_2 in a variety of combustion systems.

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TABLE I. FLAME-BAND CALIBRATION EXPERIMENTS

Mixture[a]	T	Total Concentration (10^{18} molec/cm^3)	$[O]_{P.E.}$[b] (10^{16} molec/cm^3)	$[CO]_{P.E.}$[b] (10^{17} molec/cm^3)	Signal (Volts)	$\frac{\text{Signal}}{[O]_{P.E.}\,[CO]_{P.E.}}$ (10^{-34} V cm^6 molec.$^{-2}$)
A	2035	1.44	1.56	1.70	0.37	1.39
3.95% O_2	2245	1.52	1.65	1.86	0.45	1.47
4.17% H_2	2260	1.53	1.66	1.87	0.49	1.58
12.02% CO	2345	1.51	1.64	1.87	0.48	1.57
9.44% CO_2	2470	1.51	1.63	1.89	0.55	1.78
	2540	1.57	1.68	1.99	0.56	1.66
	2670	1.52	1.63	1.93	0.54	1.72
	2690	1.56	1.69	1.99	0.61	1.81
B	1970	2.52	1.36	1.45	0.30	1.52
1.96% O_2	2060	2.66	1.44	1.56	0.31	1.38
2.06% H_2	2205	2.74	1.48	1.64	0.36	1.48
5.95% CO	2230	2.82	1.53	1.70	0.38	1.46
4.67% CO_2	2415	2.80	1.50	1.73	0.43	1.65
	2475	3.07	1.64	1.90	0.49	1.56
	2620	2.98	1.57	1.88	0.51	1.74
	2745	2.75	1.43	1.74	0.51	2.05

[a]Balance was Argon.

[b]Computed partial-equilibrium values.

TABLE II. SUMMARY OF EXPERIMENTAL OBSERVATIONS (O_2 SYSTEM)

Mixture[a]	T(K)	Concentration (10^{18} molec/cm^3)	Flame-Band Signal			CO_2 Signal		
			t_i (μsec)[b]	λ (μsec^{-1})[c]	V_{max} (volts)[d]	t_i (μsec)[e]	t' (μsec)[f]	t^* (μsec)[g]
C	2050	4.42	136	-	0.44	130	195	375
0.049% H_2	2140	4.52	107	-	0.49	102	165	320
1.01% O_2	2250	4.60	75	-	0.54	75	120	237
3.28% CO	2355	4.69	66	-	0.56	62	105	225
	2560	4.84	43	-	0.70	39	64	126
	2620	4.87	36	-	0.71	35	57	115
	2675	4.95	32	-	0.72	34	55	112
	2765	4.96	26	-	0.76	24	44	94
	2810	4.99	25	-	-	26	46	100
D	2070	4.95	57	.073	3.1	78	108	185
0.050% H_2	2160	5.07	47	.100	3.3	60	84	143
1.00% O_2	2215	5.10	43	.108	3.4	54	78	137
12.17% CO	2215	5.11	38	.089	3.5	53	76	130
	2325	5.21	26	.109	3.8	42	58	98
	2375	5.24	27	.110	3.8	41	58	100
	2475	5.34	16	.110	4.1	32	45	80
	2565	5.38	16	.149	4.3	29	42	75
	2625	5.45	15	.164	4.5	23	35	60
	2700	5.49	12	.160	4.4	23	35	63
	2740	5.55	5	.144	4.5	16	27	50
	2820	5.55	4	.154	4.8	17	26	48
	2870	5.63	11	-	5.0	15	24	45

[a] Balance was Argon.
[b] Time relative to t_o (see text) when signal = 0.02V.
[c] d ℓn (signal)/dt
[d] Plateau signal.
[e] Time relative to t_{mp} (see text) at which tangent to $[CO_2]$-time plot intercepts t-axis.
[f] For Mixture C, time relative to t_{mp} (see text) when $[CO_2] = 8.0 \times 10^{15}$ molecule/cm^3. For D, time when $[CO_2] = 1.0 \times 10^{16}$.
[g] For C, time (see [f]) when $[CO_2] = 2.4 \times 10^{16}$. For D, time when $[CO_2] = 3.0 \times 10^{16}$.

TABLE III. SUMMARY OF EXPERIMENTAL OBSERVATIONS (N_2O SYSTEM)

		Concentration	Flame-Band Signal		CO_2 Signal	
Mixture[a]	T(K)	(10^{18} molec./cm^3)	$t_{\frac{1}{2}}$ (μsec)[b]	V_{max} (volts)[c]	t' (μsec)[d]	t'' (μsec)[e]
E	1930	4.39	98	.09	72	123
0.050% H_2	2045	4.49	39	.11	46	90
1.01% N_2O	2090	4.56	28	.13	38	77
2.99% CO	2150	4.57	22	.18	18	55
	2255	4.69	15	.24	20	47
	2285	4.70	22	.24	23	52
	2380	4.79	15	.32	12	43
	2440	4.83	16	.38	13	50
	2470	4.96	14	.45	13	40
	2545	4.89	12	.44	8	40
	2635	4.95	8	.58	--	70
	2750	5.08	9	.64	11	140
	2765	5.05	10	.60	12	180
F	2030	4.95	32	.50	30	71
0.049% H_2	2065	5.01	31	.73	25	58
1.04% N_2O	2210	5.19	20	1.10	15	42
12.01% CO	2235	5.18	15	1.35	13	35
	2305	5.22	19	1.45	14	37
	2360	5.32	15	1.72	11	37
	2420	5.38	12	1.95	10	33
	2535	5.48	10	2.25	8	75
	2605	5.54	9	2.70	9	118
	2720	5.63	7	3.10	8	250
	2845	5.70	7	3.90	6	235

[a] Balance was Argon.
[b] Time relative to t_o (see text) when signal = ½ plateau value.
[c] Plateau signal.
[d] For Mixture E, time relative to t_{mp} (see text) when $[CO_2] = 4 \times 10^{15}$ molecules/cm^3. For F, time when $[CO_2] = 5 \times 10^{15}$.
[e] For Mixture E, time relative to t_{mp} when $[CO_2] = 1.0 \times 10^{16}$. For F, time when $[CO_2] = 2.0 \times 10^{16}$.

TABLE IV. MECHANISM AND RATE CONSTANTS FOR THE O_2 SYSTEM

	Reaction	Rate Constant[a] A	E_a	Reference
1.	$CO + O_2 = CO_2 + O$	5.8 E - 12	210	2
2.	$O + H_2 = OH + H$	3.6 E - 10	57	13
3.	$OH + H_2 = H_2O + H$	3.6 E - 11	22	15
4.	$H + O_2 = OH + O$	2.0 E - 07 $T^{-.91}$	70	16
5.	$OH + CO = CO_2 + H$	6.7 E - 12	33	3
6.	$CO + O + M = CO_2 + M$	1.6 E - 34	0	11

[a]Expressed in Arrhenius form, $k = A\exp(-E_a/RT)$, A in cm-molecule-sec units, E_a in kJ/mol.

TABLE V. MECHANISM AND RATE CONSTANTS FOR THE N_2O SYSTEM

	Reaction	Rate Constant[a] A	E_a	Reference
1'	$N_2O + M = N_2 + O + M$	2.7 E - 10	216	See text
2'	$O + N_2O = 2NO$	7.7 E - 11	117	11
3'	$O + N_2O = N_2 + O_2$	7.7 E - 11	117	11
2	$O + H_2 = H_2O + H$	3.6 E - 10	57	13
3	$OH + H_2 = H_2O + H$	3.6 E - 11	22	15
4	$H + O_2 = OH + O$	2.0 E-07 $T^{-.91}$	70	16
5	$OH + CO = CO_2 + H$	6.7 E - 12	33	3
6	$CO + O + M = CO_2 + M$	1.6 E - 34	0	11
4'	$H + N_2O = N_2 + OH$	See text		

[a]See Table IV.

LEGENDS

Figure 1. Arrhenius plot of flame-band calibration data. ○ = Mixture A; here the total concentration was near 1.5×10^{18} molecule/cm^3. □ = Mixture B; here the concentration was near 2.9×10^{18}.

Figure 2. Flame-band data for the O_2 system. (a) Induction Times: ○ = Mixture C; □ = Mixture D. (b) Exponential Growth Rates: □ = Mixture D. (c) Plateau Voltages: ○ = Mixture C; □ = Mixture D. In all cases, the solid symbols are the calculated values. All times are relative to t_o (see text).

Figure 3. Flame-band data for the N_2O system. (a) Time required to reach one-half the plateau voltage: ○ = Mixture E; □ = Mixture F. (b) Plateau Voltages: ○ = Mixture E; □ = Mixture F. Solid symbols are the calculated values. All times are relative to t_o (see text).

Figure 4. CO_2 data for the O_2 system. (a) Induction Times: ○ = Mixture C; □ = Mixture D. (b) Mixture C: △ = time when $[CO_2] = 8.0 \times 10^{15}$ molecule/cm^3; ▽ = time when $[CO_2] = 2.4 \times 10^{16}$. (c) Mixture D: △ = time $[CO_2] = 1.0 \times 10^{16}$; ▽ = time $[CO_2] = 3.0 \times 10^{16}$. Solid symbols are calculated values. All times are relative to t_{mp} (see text).

Figure 5. CO_2 data for the N_2O system. (a) Mixture E: ○ = time $[CO_2] = 4.0 \times 10^{15}$ molecule/cm^3; □ = time $[CO_2] = 1.0 \times 10^{16}$. (b) Mixture F: △ = time $[CO_2] = 5.0 \times 10^{15}$; ▽ = time $[CO_2] = 2.0 \times 10^{16}$. The solid symbols are calculated values. All times are relative to t_{mp} (see text).

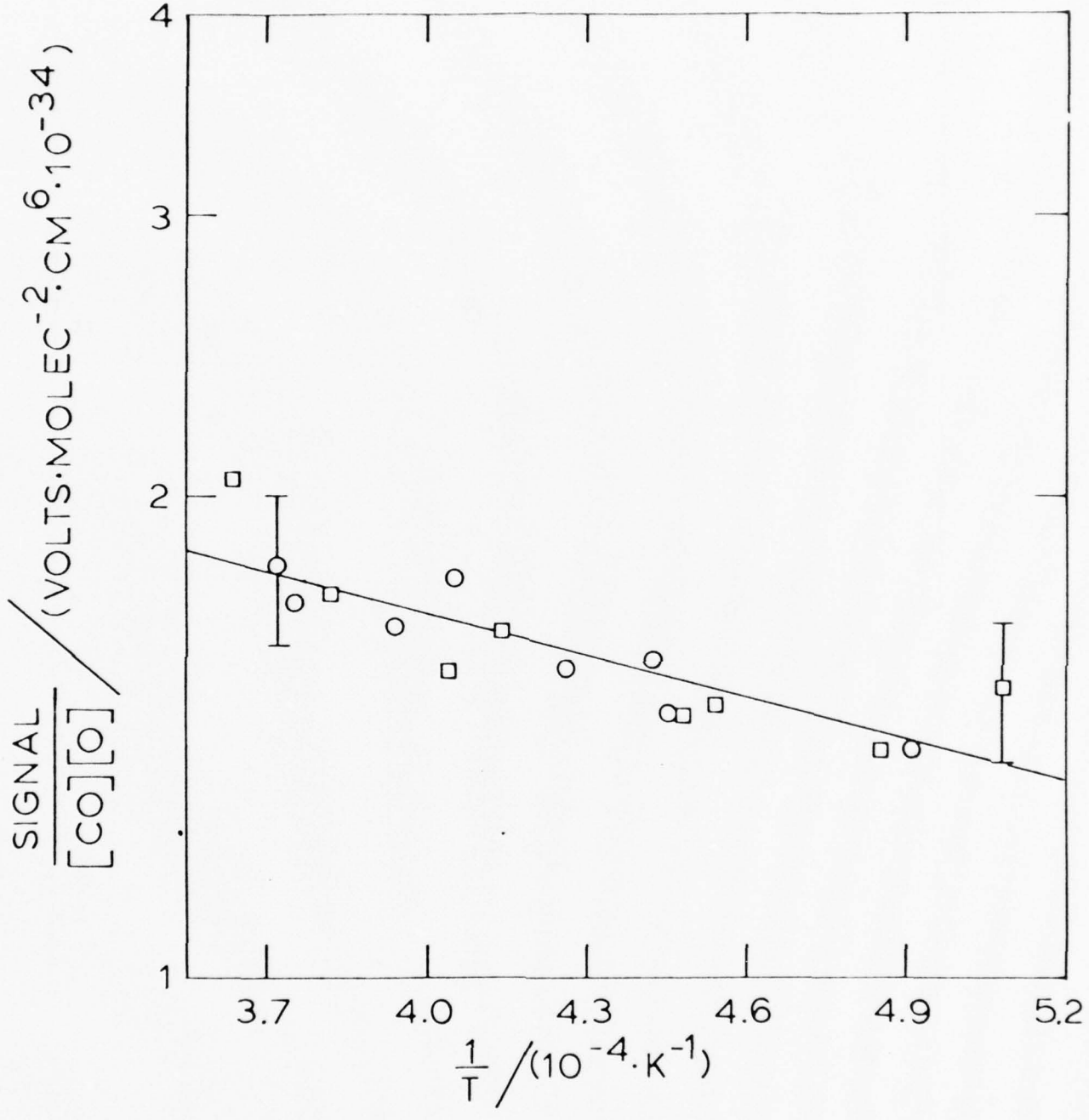


Fig. 1

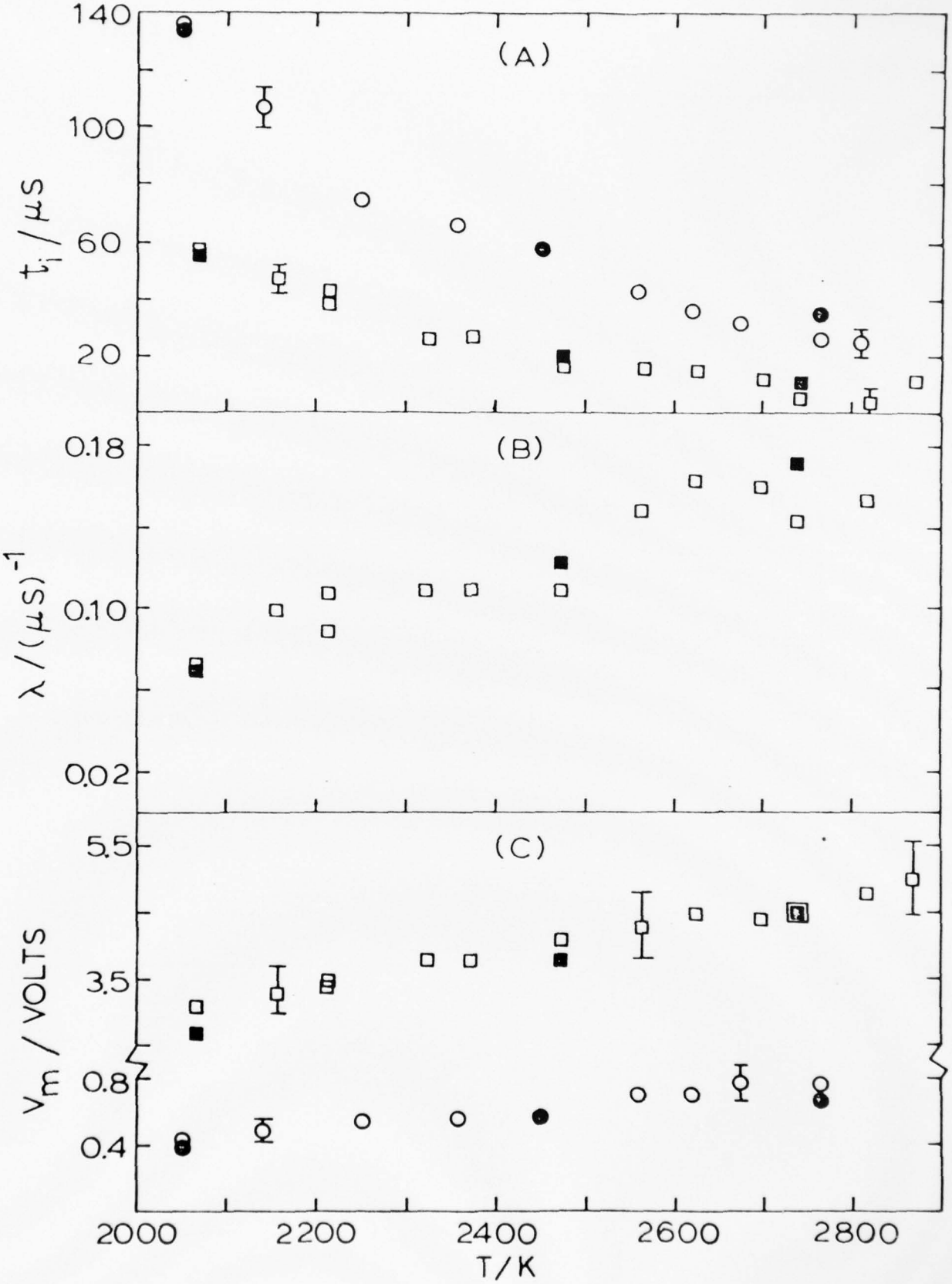
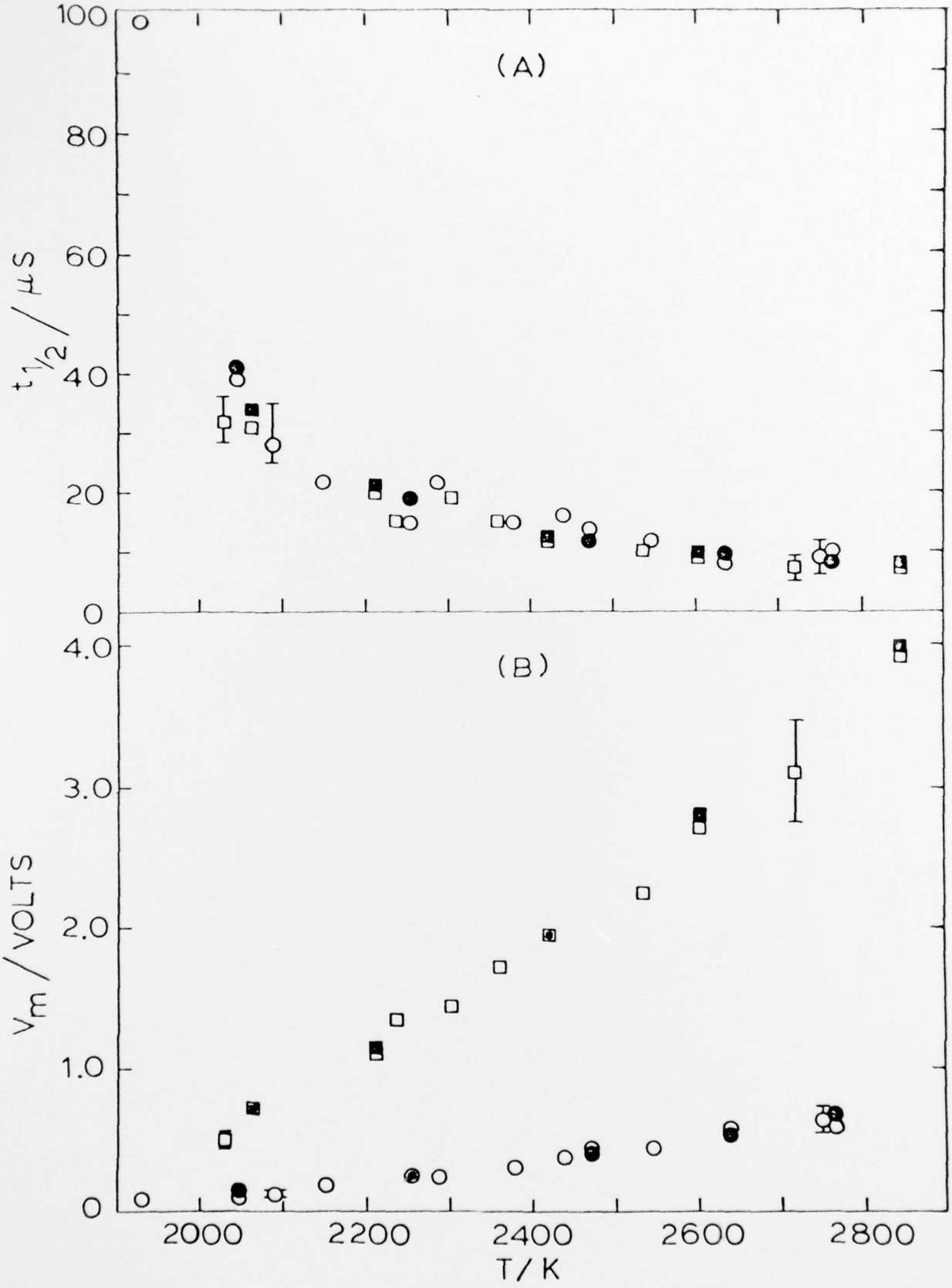

140
100
60
20
t_i / μs
(A)
0.18
0.10
0.02
λ / (μs)$^{-1}$
(B)
5.5
3.5
0.8
0.4
V_m / VOLTS
(C)
2000
2200
2400
2600
2800
T/K

Fig. 2


(A)
$t_{1/2}$ / μs
100
80
60
40
20
0
(B)
V_m / VOLTS
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3.0
2.0
1.0
0
2000
2200
2400
2600
2800
T / K

Fig. 3

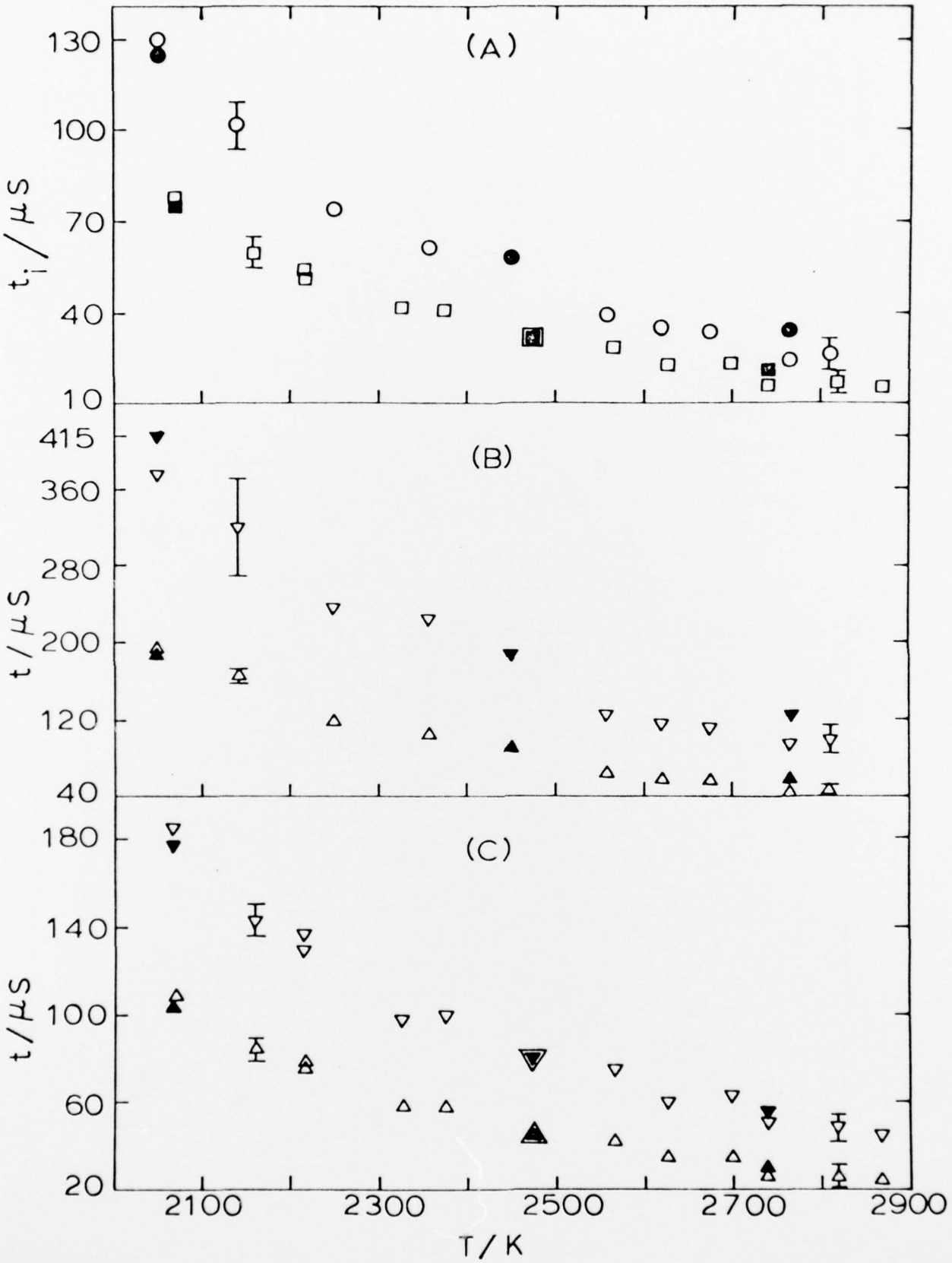
(A)
(B)
(C)
$t_i/\mu s$
$t/\mu s$
T/K
130
100
70
40
10
415
360
280
200
120
40
180
140
100
60
20
2100
2300
2500
2700
2900

Fig. 4

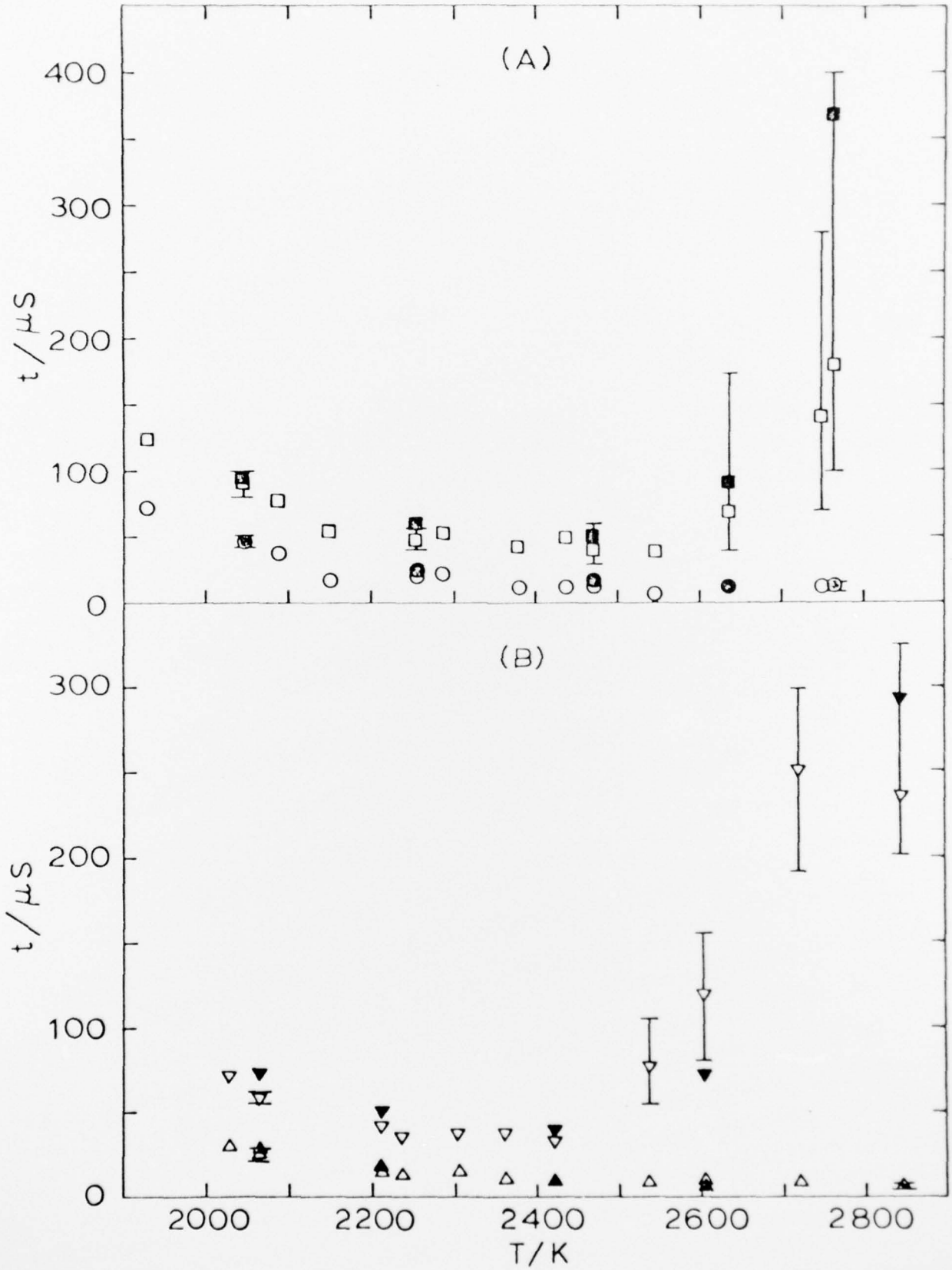
(A)
400
300
200
100
0
t/μs
(B)
300
200
100
0
t/μs
2000
2200
2400
2600
2800
T/K

Fig. 5

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Shock Tube

H_2/O_2 System

H_2/N_2O System

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Emissions at 450 nm and 4.27 μm have been measured when a variety of mixtures containing H_2, CO, either O_2 or N_2O, and Ar were heated behind reflected shock waves to temperatures of 2000-2850 K and total concentrations near 5×10^{18} molecule/cm^3. These emissions were used to obtain absolute concentration - time data for both oxygen atoms and carbon dioxide. The data were then compared to the results of numerical integrations of the likely mechanisms. It was observed that quantitative agreement between calculations and observations were obtained for the $H_2/CO/O_2/Ar$ system using

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recent high temperature literature rate constants. For the $H_2/CO/N_2O/Ar$ system, the rate constant for the reaction:

$$H + N_2O \rightarrow N_2 + OH$$

was adjusted so as to fit the data. Here it was found that a good fit to both [O] and [CO_2] profiles could be achieved with $k = 3.0 \times 10^{-9} \exp(-113 kJ/RT)$ cm^3 $molecule^{-1}$ s^{-1}. Comparison to data at lower temperatures suggests that this might be another example of a "non-Arrhenius" rate constant. The implications of these results to studies of hydrocarbon oxidation are discussed.